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13. ABSTRACT *(Maximum 200 words)*

Robust models for predicting high temperature/pressure thermal expansion for a range of solids have been developed. The inter-relationships between several thermophysical properties including thermal expansion, specific heat, elastic properties, and self-diffusion of materials has been investigated. The role of defects on thermal expansion at high temperature and pressure has also been explored. During the course of the project several models for thermal expansion were developed extending earlier work of Reeber. The product of thermal expansion, bulk modulus, and volume has been shown to approach a constant at high temperatures for alkali halides, rare earth oxides, fcc metals, and ZnS. Models have been applied to investigate high temperature thermal expansion of alkali halides, rare earth oxides, group IV elements, fcc metals, bcc metals, SiC, III-V and II-VI compounds. Analytical expressions have been provided that represent the thermal expansion of these materials from near 0 K to the melting point. Models have also been extended to high pressure thermal expansion of MgO, NaCl, Group IV elements, and W. The bulk modulus and self-diffusion for W and Ta have been predicted to their melting points.

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Crystal Chemistry of Ceramic/Mineral Systems

Final Report

Robert R. Reeber

January 16, 1997

U.S. Army Research Office

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A. Research Objectives:

The objectives of this work were twofold (1) to develop x-ray diffraction techniques, from an experimental and analytical standpoint, for Laue and continuous x-ray methods; and 2) to model and predict physical and crystallochemical properties of isostructural inorganic compounds with emphasis on thermal expansion, phase transitions and mechanical properties.

B. Summary of Most Important Results:

Significant progress was made on analytical interpretation of Laue photographs and a Laue program written in Fortran was completed. CdZnCaBaCu perovskites were synthesized by reacting and oxidizing selenides and sulfides of Cd and Zn with a CaBaCu precursor. The materials were evaluated for superconducting properties and, although structurally related to high Tc superconductors, showed no indication of superconductivity above 77 K. A single phase CaBaCu oxide material was identified as orthorhombic PMNA space group.

The main emphasis of the work concentrated on Objective 2), which was in concert with Mr. Wang's doctoral thesis. This objective, to model and predict physical and crystallochemical properties of isostructural inorganic compounds, was so successful that the scope was extended to include refractory metals and group IV semiconductors including diamond.

Robust models for predicting high temperature/pressure thermal expansion for a range of solids have been developed. The inter-relationships between several thermophysical properties including thermal expansion, specific heat, elastic properties, and self-diffusion of materials was investigated. The role of defects on thermal expansion at high temperature and pressure was modeled theoretically. Exact expressions for these properties were provided that are in excellent agreement with existing experimental data.

During the course of the project several models for thermal expansion were developed that extended earlier work of Reeber. The product of thermal expansion, bulk modulus, and volume has been shown to approach a constant at high temperatures for alkali halides, rare earth oxides, fcc metals, and ZnS. The work has been applied to model and predict high temperature thermal expansion of alkali halides, rare earth oxides, group IV elements, fcc metals, bcc metals, SiC, III-V and II-VI compounds.

Analytical expressions have been provided that represent the thermal expansion of these materials from near 0 K to the melting point. The models have been extended to predict high pressure thermal expansion of MgO, NaCl, Group IV elements, and W. The bulk modulus and self-diffusion for W and Ta have been predicted to their melting points. Variation of thermal expansion and strength with pressure/temperature for diamond and tungsten has also been studied. One report, a PhD dissertation, and fourteen peer reviewed papers were accepted and published during the course of the research. The models developed will have impacts on both materials science and mineral physics.

Work on tungsten and diamond was presented at the 20th Army Science Conference and was awarded a certificate as the best poster paper of its session. The bulk moduli predictions for tungsten and tantalum was given as a poster paper at the Army/University of Michigan Workshop on Hot Gas Erosion of Materials. Requests for the results of both papers were received from Dr. John Vasilakis, Army Large Caliber Research Facility at Watervliet Arsenal , Watervliet, NY.

C. Publication List:

Dissertation:

Wang, Kai, **Thermal Expansion and thermophysical properties of materials and minerals at high temperature and high pressure,** University of North Carolina-CH December 1995.

1. Reeber, R. R., Surface engineering of structural ceramics, *J. Am. Ceram. Soc.*, **76**, 261-268, 1993.
2. Wang, K. and R. R. Reeber, Thermal defects and thermal expansion of ionic crystals at high temperatures, *phys. stat. sol. (a)*, **146**, 621-627, 1994.
3. Wang, K. and R. R. Reeber, Thermal expansion of caesium halides with the CsCl structure, *J. Appl. Cryst.*, **28**, 306-313, 1995.
4. Wang, K. and R. R. Reeber, High temperature thermal expansion of alkali halides, *J. Phys. Chem. Solids*, **56**, 895-900, 1995.
5. Reeber, R. R., K. Goessel, and K. Wang, Thermal expansion and molar volume of MgO, periclase, from 5 to 3000 K, *Eur. J. Mineral.*, **7**, 1039-1047, 1995.
6. Wang, K. and R. R. Reeber, A simplified model for predicting high pressure thermal expansion of MgO, *Geophys. Res. Lett.*, **22**, 1297-1300, 1995.
7. Reeber, R. R. and K. Wang, Thermal Expansion of β-SiC, GaP and InP, *Mat. Res. Soc. Symp. Proc.*, **410**, 211-216, 1996.
8. Reeber, R. R. and K. Wang, Thermal expansion and lattice parameters of Group IV semiconductors, *Mat. Chem. Phys.*, **46**, 259-264 (1996).
9. Reeber, R. R. and K. Wang, Thermal expansion, molar volume and specific heat of diamond from 0 to 3000 K, *J Elect. Mat.*, **25**(1), 63-67, 1996.
10. Wang, K. and R. R. Reeber, Thermal expansion of copper, *High Temp. Mat. Sci.*, **35**, 181-186, 1996.
11. Wang, K. and R. R. Reeber, Thermal expansion of alkali halides at high pressure: NaCl as an example, *Phys. Chem. Minerals*, **23**, 354-360, 1996.
12. Wang, K. and R. R. Reeber, A model for evaluating and predicting high temperature thermal expansion, *J. Mat. Res.*, **11**(7), 1800-1803, 1996.
13. Reeber, R. R. and K. Wang, High temperature/pressure thermal expansion of elemental semiconductors and tungsten, *Proceedings of The 20th Army Science Conference*, Norfolk, VA, (June, 1996)
14. Wang, K. and R. R. Reeber, High temperature bulk moduli and self-diffusion for tantalum

and tungsten, *High Temp. Mat. Sci.*, (in press, 1996).

15. Reeber, Robert R. Final Report, Short Term Sabbatical Research January 19, 1994.

Talks at Professional Meetings:

Wang, K. and R. R. Reeber, High temperature thermal expansion, bulk moduli and self-diffusion for tantalum and tungsten, *Army Research Office-University of Michigan Workshop on Hot Gas Erosion and Wear of Materials*, Ann Arbor, Michigan, September, 1996.

Reeber, R. R. and K. Wang, High temperature/pressure expansion of elemental semiconductors and tungsten, *20th Army Science Conference, Norfolk, Virginia*, June, 1996

Wang, K. and R. R. Reeber, Estimation of high temperature thermal expansion for some minerals-a lower limit, *Spring AGU Meeting, EOS*, 77(17), S145, 1996.

Reeber, R. R., Elastic Constants of Diamond, *International Symposium on Manufacturing Practices and Technologies and the Joint Fall Meetings of the Basic Science, Electronics, Glass & Optical Materials and Nuclear & Environmental Technologies Divisions Abstract Book*, New Orleans, La., Nov. 5-8, 1995. ???

Reeber, R. R. and K. Wang, Corresponding States Predictions for Thermal Expansion of Group IIA Metal Oxides, *International Symposium on Manufacturing Practices and Technologies and the Joint Fall Meetings of the Basic Science, Electronics, Glass & Optical Materials and Nuclear & Environmental Technologies Divisions Abstract Book*, New Orleans, La., Nov. 5-8, 3-BP-95F, 29, 1995.

Reeber, R. R. and K. Wang, Thermal Expansion of β-SiC, and some other Grimm-Sommerfeld crystals at high temperature, *Proceedings of the Materials Research Society Fall Meeting*, Abstracts, 533, 1995.

Wang, K. and R. R. Reeber, A model for evaluating and predicting high temperature thermal expansion, *Proceedings of the Materials Research Society-NC Section Annual Symposium*, November, 1995.

Wang, K. and R. R. Reeber, A simplified model for predicting high pressure thermal expansion of MgO, *Proceedings of the IUGG XXI General Assembly,* Boulder, Colorado, Abstracts Week A, A355, 1995.

Wang, K. and R. R. Reeber, A simplified model for predicting high pressure thermal expansion of alkali halides, *Spring AGU Meeting, EOS*, 76(17), S276, 1995.

Reeber, R. R. and K. Wang, Thermal expansion of diamond, *TMS Meeting, J. of Metals*, **46**, 184, 1994.

Reeber, R. R., K. Wang, and E. A. Smelik, Phase transitions, twinning and crystal growth studies with a travel Laue camera, *European High Resolution X-ray Diffraction Symposium*, Abstract Book, Gosen, Germany. 1994.

Reeber, R. R. and K. Wang, Thermal expansion and lattice parameters of MgO, periclase, from 5 to 2900 K, *Eur. J. Mineral.*, **6**, 222, 1994.

Reeber, R. R. and K. Wang, Computer indexing of high and low symmetry Laue patterns, *Amer. Cryst. Assoc. Ann. Meeting Proceedings*, **22**, Series 2, 149, 1994.

Wang, K. and R. R. Reeber, Thermal expansion of alkali halide structure type crystals at high temperature, *Spring AGU Meeting, EOS*, 75(16), 187, 1994.

Reeber, R. R. and K. Goessel, Thermal expansion and molar volume of MgO, periclase, *Spring AGU Meeting, EOS*, **74**, 162, 1993.

D. Participating Scientific Personnel

Dr. Robert R. Reeber, Adjunct Professor
Mr. Kai Wang graduate student assistant PhD Dissertation completed December 1995.
Dr. Helmut Klapper, Professor, University of Bonn, Germany (4 weeks)
Professor James Waber, visiting researcher (4 weeks)
Kathryn Goessel (undergraduate geology major)
Richard Dixon (undergraduate chemistry major)
Mr. Peter Mihok graduate assistant (1 month)

5. Report of Inventions: None

Appendix 1 Abstracts of Papers Listed in Part C.

1. The role of surface engineering for controlling structural ceramic properties is reviewed. Initially, a perspective of the effects of an unmodified surface state on fracture, adhesion, tribological properties, and degradation is given. Ceramic surface modification techniques including laser, ion, ion-beam-assisted deposition, and plasma-assisted deposition are then discussed with regard to how each non-equilibrium technique affects bulk and surface properties. The importance of experiments, process and materials characterization, and modeling for understanding changes in localized bonding, chemistry, and structure is emphasized. Although not exhaustive, a broad guide to important literature is given.

2. Thermal expansion of ionic crystals at high temperature has been treated as contributions from the perfect crystal and its lattice thermal defects. In this paper, a semi-empirical quasi-harmonic model[1,2] represents the thermal expansion of the perfect crystal, and contributions from lattice defects at high temperature are described by the theory of thermodynamics of point defects. The formation energies of thermal defects of those crystals considered have been obtained from fitting thermal expansion differences between real and perfect crystals. Results show that there is a linear trend between the formation energies of thermal lattice defects and their Debye temperatures. The formation energies obtained are smaller than theoretical calculations and ionic conductivity measurements. This indicates thermal defects are ordered at high temperatures.

3. Low temperature caesium halides thermal expansion has been approximated by a quasi-harmonic approach (QHM) [Reeber(1975), *phys. stat. sol. (a)*, **32**, 321-331; Reeber & Haas(1984), *Thermal Expansion*, **8**, 31-48] and predicted at high temperature with a modified quasi-harmonic model (MQHM) [Wang & Reeber(1994a), submitted to *J. Phys. Chem. Solids*]. Formation enthalpies of high temperature defects have also been obtained by fitting lattice differences between a real and an approximate perfect crystal (QHM).

Typical values of the coefficients of thermal expansion and lattice parameters are given.

4. Thermal expansion data for eleven sodium chloride structure-type solids have been evaluated with an empirical modified quasi-harmonic model for thermal expansion. Earlier it was shown for Group IV elements and 10 Grimm-Sommerfeld compounds that an empirical quasi-harmonic model fits experimental data from nearly zero to intermediate temperatures in the vicinity of T_L, the approximate temperature, where all lattice modes are fully excited. At higher temperatures, experimentally measured thermal expansion is slightly higher than an extrapolation of this empirical relationship. The difference can be approximated with a second-order term that gives excellent quantitative agreement with experiment for the available data to approximately 90% of the melting temperature.

5. Thermal expansion and molar volume of periclase are important parameters for thermodynamic modeling of the earth's interior. We have critically reviewed the available data and have found wide variations in the literature for MgO lattice parameters at room and high temperatures. Earlier Reeber (1975) developed an empirical quasi-harmonic model (QHM) that provides an excellent representation of thermal expansion from near 0 to 1200K. Wang and Reeber (1995a) show for alkali halides that above a temperature T_L, the approximate temperature where all lattice modes are effectively excited, experimentally measured thermal expansion is slightly higher than an extrapolation of this empirical relationship. This difference is approximated with a 2nd order term that gives excellent quantitative agreement with experiment for alkali halides and cesium halides (Wang and Reeber, 1995b) to approximately 90% of the melting temperature. The existing literature for periclase is evaluated within the constraints of the modified quasi-harmonic model (MQHM) and x-ray measurements at room temperature. At very high temperatures where experimental data is not available the MQHM provides a method to estimate high temperature thermal expansion. Our best estimate of lattice parameter at 0K is 4.20565Å and at 298K 4.21154Å.

6. Thermal expansion of MgO, periclase, is approximated by contributions from a quasi-harmonic perfect crystal and its equilibrium high temperature/pressure defects. We demonstrate that the influence of thermal defects on high pressure thermal expansion is very small and may be neglected at lower mantle conditions. Following that, a simple relationship has been obtained between high pressure thermal expansion and the thermal expansion of a quasi-harmonic perfect crystal at zero pressure. Our estimation of MgO thermal expansion at the core-mantle boundary is $9.36 \times 10^{-6} K^{-1}$.

7. Thermal expansion is important for predicting residual stresses in epitaxial films, composites and electronic devices as well as for providing information relevant to an understanding of interatomic potentials and the equation of state of materials. Model calculations have many assumptions, both inherent and implicit, and have difficulty accurately representing thermal expansion at high temperatures and pressures. We utilize a semi-empirical quasi-harmonic model to evaluate available data for β-silicon carbide,

gallium phosphide and indium phosphide. The model allows prediction of the thermal properties of these semiconductors from near o K to the vicinity of their melting points. The approach, consisting of a simplified frequency spectrum with several Einstein terms, provides a convenient mathematical method where a minimum of empirical parameters represent the thermal property.

8.   Thermal expansion is practically and theoretically important for predicting residual stresses in epitaxial films and electronic devices as well as for providing information about the anharmonic properties of materials, and determining their equation of state. Model calculation have had difficulty in accurately representing thermal expansion at high temperatures where such considerations are most important. We utilize a semi-empirical quasi-harmonic model to evaluate available data for silicon and germanium. The model allows us to predict the thermal properties of these semiconductors from near 0K to the vicinity of their melting points. The approach, consisting of a simplified frequency spectrum with several Einstein terms, provides a convenient mathematical method where a minimum of empirical parameters represent the thermal property.

9.   Thermal expansion is of both practical and theoretical importance and it together with specific heat is essential for predicting a thermodynamic equation of state. We utilize a semi-empirical quasi-harmonic model to evaluate available data for diamond. The model allow us to predict the thermal properties of the metastable diamond polymorph to 3000K. The approach consisting of a simplified frequency spectrum with several Einstein terms provides a convenient mathematical method where a minimum of empirical parameters represent the thermal property.

10. The product of thermal expansion, bulk modulus, and volume, $\alpha_V K_T V$, is the partial temperature derivative of the work done by thermal pressure. For copper this thermodynamic product resembles a specific heat (C_V) curve and approaches a constant at high temperature. Our recent developed model utilizes available data for this parameter and recommends new copper thermal expansion values from 0 K to the melting point.

11. Thermal defects in ionic materials can have important effects on their thermal expansion at high temperatures. Earlier treatments of thermal expansion generally have neglected or not considered such effects. Here an analytical expression for the thermal defect contribution and its dependence on pressure is derived. We show that such contributions, whcih are significant at high temperature and atmospheric pressure, become negligible at pressures above approximately 0.25 to 0.35 of the bulk modulus at standard conditions. At very high pressure, based on Birch's (1968) relationship between high and low pressure thermal expansion, and assuming αK_T is independent of pressure, NaCl thermal expansion can be calculated within the constraints of a semi-empirical quasi-harmonic perfect crystal model. The calculations are compared with available theoretical and experimental values over an extented temperature/pressure regime. The method should have broad applicability for other ionic crystals.

12. In this paper, a new set of experimental data, $\alpha_V K_T V$, representing the partial temperature derivative of the work done by the thermal pressure of solid, is fitted by n-terms of a modified Einstein model. Experimental data show that $\alpha_V K_T V$, not $\alpha_V K_T$, approaches a constant value at high temperature. Based on the observed linear relationship of isothermal bulk modulus with temperature at high temperature, thermal expansion can be evaluated by fitting $\alpha_V K_T V$ data. Our previous results have shown that at low temperature or for materials with less variable bulk modulus and expansivity, thermal expansion data can be simply approximated by an n term Einstein model. More generally and for many materials, $\alpha_V K_T V$ data resembles an isochoric specific heat curve. With this method, thermal expansion can be predicted at high temperature from low and intermediate temperature range data. With accurate thermal expansion data, high temperature bulk moduli can also be predicted.

13. Thermal expansion at high temperatures and pressures is an excellent predictor of ultimate strength. Theoretical treatments have not been successful for accurately predicting thermal expansion at high temperatures. Here we approximate the thermal expansion of group IV semiconductors and tungsten by contributions from a quasi-harmonic perfect crystal and its equilibrium high temperature/pressure defects. At higher pressures thermal defect effects are small and may be neglected. The thermal expansion for each element is calculated from 0K to its respective melting point and for range of pressure from 0 GPa to 150 GPa. It is anticipated that an understanding of thermal defect behavior as a function of temperature and pressure, when contrasted with equivalent shock experiments, will provide insights for modeling and design of improved penetrator materials.

14. The tungsten bulk modulus is calculated from self-diffusion, thermal expansion and specific heat data. Our estimate of the adiabatic bulk modulus as a function of temperature is about 8% higher than earlier results at the highest temperature. For tantalum, self-diffusion coefficients are calculated from high temperature thermoelastic data. Comparisons with available experimental results and earlier calculations are provided.